MAJOR VOLATILES FROM MSL SAM EVOLVED GAS ANALYSES: YELLOWKNIFE BAY THROUGH LOWER MOUNT SHARP.
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Introduction: The Sample Analysis at Mars (SAM) and Chemistry and Mineralogy (CheMin) instruments on the Mars Science Laboratory (MSL) analysed several subsamples of <150 µm fines from five sites at Gale Crater. Three were in Yellowknife Bay: the Rocknest aeolian bedform ("RN") and drilled Sheepbed mudstone from sites John Klein ("JK") and Cumberland ("CB"). One was drilled from the Windjana ("WJ") site on a sandstone of the Kimberly formation investigated on route to Mount Sharp. Another was drilled from the Confidence Hills ("CH") site on a sandstone of the Murray Formation at the base of Mt. Sharp (Pahrump Hills). Outcrops are sedimentary rocks that are largely of fluvial or lacustrine origin, with minor aeolian deposits [1,2]. SAM's evolved gas analysis (EGA) mass spectrometry detected H_2O, CO_2, O_2, H_2, SO_2, H_2S, HCl, NO, and other trace gases, including organic fragments [3]. The identity and evolution temperature (T) of evolved gases can support CheMin mineral detection and place constraints on trace volatile-bearing phases or phases difficult to characterize with XRD (e.g., X-ray amorphous phases). They can also give constraints on sample organic chemistry. Here, we discuss trends in major evolved volatiles from SAM EGA analyses to date.

Methods: Fines were heated to ~835-900°C depending on the run, at 35°C/min, under ~25 mb of He. Evolved gases were carried in helium at ~0.8 sccm to the QMS. To investigate aspects of the flight SAM data, several laboratory systems are used to characterize analogs under SAM-like conditions.

***H_2O*:** Water was the most abundant volatile evolved from RN, JK and CB [4,5]. The overall shape of the H_2O traces is similar for all samples, except for the high T evolution near 750°C for JK and CB and the shoulder at ~450°C in the CH trace (Fig. 1). Most H_2O comes off in a wide peak <~450°C. This H_2O has many potential sources, including adsorbed H_2O, smectite interlayer H_2O, H_2O/OH from bassanite and akaganeite (identified by CheMin in some samples), H_2O from minor hydrated minerals like oxychlorine phases (inferred from SAM) and H_2O/OH from amorphous phases (CheMin detected ~30 wt% amorphous material in all samples [6-9]). The shoulder at ~450°C in the CH trace likely results mainly from dehyroxylation of the <1 wt % jarosite detected by CheMin [9]. The ~750°C peak in CB and JK traces results from the dehydroxylation of the ~20 wt % smectite clay detected by CheMin. Comparison with SAM-like lab data indicates that a trioctahedral smectite, such as Fe-saponite, is most consistent with the high T H_2O observed, consistent with CheMin observations [10].

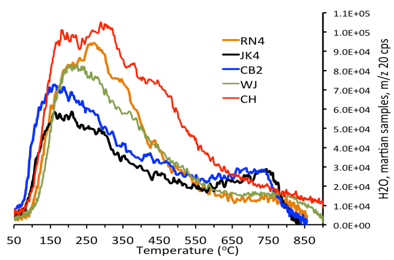

Figure 1. Sample H_2O EGA-MS traces.

Although ~10 wt % of an ~10 Å phyllosilicate was inferred from WJ and CH CheMin data and possibly results from a collapsed smectite [8,9], SAM H_2O traces do not display a distinct high T dehydroxylation peak, though there is some H_2O being evolved at high Ts (Fig. 1). Lack of a peak may result from the lower phyllosilicate abundances compared to CB and JK.

SO_2: More SO_2 evolved from WJ and CH than CB, JK and RN. All samples evolved SO_2 from 500-800°C, but JK and CB exhibited an additional evolution near 300°C (Fig. 2). CheMin analyses revealed ~1 wt% pyrrhotite (and possibly <1 wt % pyrite in JK), and several wt% Ca sulfates (which do not typically decompose in the SAM T range) [6]. The ~300°C SO_2 evolution is coincident with an O_2 evolution and likely results from partial oxidation of the sulfide. Some SO_2 evolved from 500–700°C also likely results from sulfide oxidation, based on analog work [11]. In RN and WJ, no sulfur minerals expected to decompose in the SAM T range were detected by CheMin. As a result, SO_2 is likely evolved from the amorphous component and potentially trace S minerals. More SO_2 evolved from WJ, implying more trace

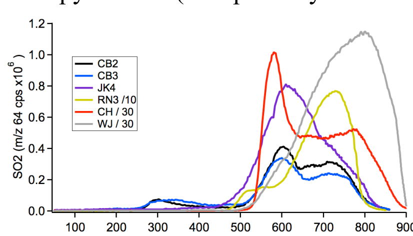

Figure 2. Sample SO_2 EGA-MS traces.

S-phases (some Fe- and Al sulfates, sulfites, sulfides evolve SO_2 at relevant Ts) or more S associated with the amorphous component. In CH, the only sulfur mineral detected was jarosite. SO_2 evolution near 580°C (Fig. 2) is consistent with SAM-like analyses of jarosite. The <1 wt% jarosite detected cannot account for all the SO_2 evolved (or detected by APXS). This SO_2, including SO_2 evolved at higher T including a ~775°C peak, must be associated with the amorphous phase and possibly with trace sulfur minerals. Some Al sulfates, for example, evolve SO_2 near 775°C and are consistent with acidic conditions needed to form jarosite.

O_2: All samples evolved O_2 at Ts below ~500°C (Fig. 3). These O_2 releases, together with detections of HCl and chlorinated hydrocarbons (not shown) are evidence of oxychlorine phases such as perchlorates or chlorates [e.g., 5]. The O_2 evolution is different for each sample. In JK there are two peaks, suggesting different phases or reactions during heating (oxidation of organic compounds, reaction with reduced Fe phases) [5]. For RN and the second JK peak, the O_2, and HCl, evolutions, are consistent with a Ca-chlorate, or Mg- or Ca-perchlorate mixed with ferrihydrite or palagonitic materials [5,12-14]. For CH, they are consistent with Mg- or Ca-perchlorate mixed with hematite or magnetite [14]. For the first JK peak, Fe perchlorates evolve O_2 at similar Ts [5]. For CB and WJ, O_2 evolutions do not match those from any common perchlorate or chlorate but mixtures with relevant minerals may shift O_2 evolution Ts [e.g. 12,14].

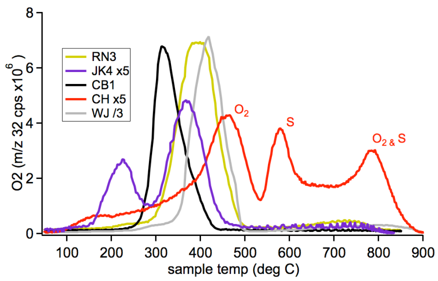

Figure 3. Sample O_2 EGA-MS traces.

In CH alone, O_2 evolution was observed near 775 °C - a higher T than expected from perchlorate or chlorate decompositions. There are several possible explanations for this including sulfate decomposition, gas-phase reactions at high T, etc., and work is ongoing.

CO_2: All samples evolved CO_2 below ~600°C. There are several possible causes. For RN, CH, and the high T shoulder of JK between ~400 and 600°C CO_2 could be related to decomposition of a fine-grained Fe/Mg carbonate [e.g., 4,5]. For JK, CB, CH, and WJ, coincidence of CO_2 and O_2 evolutions, often associated with decreases in the signal from masses associated with organic fragments, suggests combustion of organic compounds. Some of this is very likely combustion of the derivatization agent background in SAM [e.g., 5] but CO_2 from combustion of sample organics (martian or resulting from meteoritic input) could also contribute [e.g., 5]. Decarboxylation or loss of carbonyl groups of organic compounds are other potential sources [5,15]. For JK and CB, CO_2 coincident with HCl evolution may result from acid vapor dissolution of carbonates. CO_2 evolved <200°C from JK, WJ, and CH could result from adsorbed CO_2.

CH exhibits an unique high T CO_2 release at ~725°C and at ~775°C (Fig. 4) that coincides with the high T O_2 release. The co-evolution with O_2 suggests that this CO_2 could be due to the combustion of organics at high T (background organics, sample organics, or both). The ~725°C peak may result from decomposition of minor Ca carbonate, though organic combustion could also cause this peak.

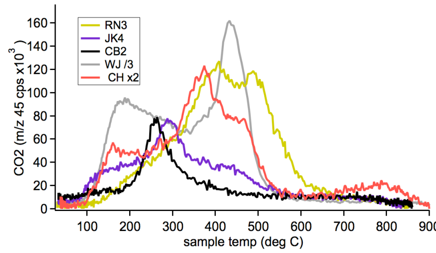

Figure 4. Sample CO_2 EGA-MS traces.

Discussion: The presence of sulfides, smectites and magnetite in the Sheepbed mudstone indicate that the bulk of the rock was relatively reduced and had experienced interaction with circumneutral alteration fluids. The CH sample from Pahrump Hills contained jarosite, but no sulfides, evolved more SO_2 than the mudstone samples, and contained more hematite than magnetite, suggesting more oxidizing conditions and some interactions with more acidic fluids. The Kimberly WJ sample also had no sulfides and evolved more SO_2 than the mudstone samples.

The possible presence of carbonate in CH, to produce some of the high T CO_2, may be unlikely if the rock interacted with acidic fluids. However, since the jarosite is minor, it is possible that it formed in a low water/rock alteration setting enabling a non-equilibrium mixture to persist. The presence of oxychlorine compounds in all samples may imply they formed by a widespread process (e.g., 16,17) somewhat independent of these sample site differences.

References: [1] Gupta, S. et al. (2014) AGU mtg [2] Grotzinger J. et al. (2014) AGU mtg [3] Freissinet, C. et al. (2015) *JGR*, in press. [4] Leshin L.A. et al. (2013) *Science, 341*(6153), 10.1126/science.1238937. [5] Ming D.W. et al. (2013) *Science*, 10.1126/science.1245267. [6] Vaniman D.T. et al. (2013) *Science*, 10.1126 /science.1243480. [7] Bish D.L. et al. (2013) *Science, 341*(6153), 10.1126 /science.1238932. [8] Rampe, E.B. et al (2014) AGU mtg [9] Cavanaugh, P.D. et al. (2015) *LPS XLVI* [10] McAdam, A.C. et al. (2014), in prep. [11] McAdam, A.C. et al. (2014) *LPS XLV* [12] Sutter, B. et al. (2014) *LPS XLV*. [13] Bruck, A et al. (2014) *LPS XLV*. [14] Sutter, .B. et al. (2015) *LPS XLVI*. [15] Eigenbrode E.L. et al. (2014) *LPS XLV*. [16] Simonaitis, R. et al. (1975) *PSS, 23*, 1567. [17] Kim, Y.S. et al. (2013) *JACS, 135*, 4910.